Growth, Assembly, and Characterization of Zinc Oxide Nanostructures

by **J. W. P. Hsu, N. C. Simmons, T. L. Sounart, J. Liu, D. A. Scrymgeour, D. A. Tallant, L. N. Brewer, J. A. Floro, and J. A. Voigt**

Motivation—ZnO nanostructures are at the forefront of nanomaterials research because of their interesting semiconducting, optical, and piezoelectric properties, combined with their relative ease of growth by various techniques. The next step in making these nanostructures useful requires assembling them on surfaces in a controlled manner. Since conventional lithography techniques are not conducive to patterning of three-dimensional nanomaterials, new approaches need to be developed.

Accomplishment—Microcontact printing was employed to form an organic template in order to direct ZnO nanorod growth from solution on Ag surfaces [Fig. 1(a)]. Solution growth utilizes environmentally benign chemistry and is compatible with the use of organic molecules to control/modify inorganic crystal growth. Organic modifiers were used to create complex ZnO nanostructures. Fig. 1(b) shows an example of these nanostructures assembled on pre-determined locations on surface.

In this experiment, it was observed that the majority of ZnO nanorods orient with the [0001] axis perpendicular to the Ag substrate. The Ag films used were polycrystalline with high (111) texture but no in-plane alignment. ZnO nanorods also display random in-plane orientations. However, when a multi-grain Ag foil was used as a substrate, preferential nucleation on [111] oriented grains was evident [Fig. 2(a)] with ZnO rods orienting perpendicular to the surface and displaying in-plane alignment (modulo 6-fold degeneracy). Since transmission electron microscopy images show that the ZnO-Ag interface is abrupt and contains no foreign materials such as AgO [Fig. 2(b)], there is definitely a crystallographic relation between ZnO and Ag.

The physical properties of these ZnO nanorods were investigated with piezoelectric force microscopy (PFM) and photoluminescence (PL). ZnO has a wurtzite crystal structure, with inversion symmetry broken in the [0001] direction and piezoelectric response parallel to that direction. Using PFM, it was established that these ZnO nanorods are oriented with <0001> directed away from the substrate (Fig. 3). Piezoelectric response was quantitatively measured and found to vary from rod to rod. This variation was not correlated with rod length or diameter. The origin is currently being investigated. PL measurements of as-grown and annealed nanorods reveal that the defects responsible for deep-level luminescence are different from those found in vapor phase grown nanostructures, are not associated with oxygen deficiency, and most likely exist in the bulk, rather than the surface, of the nanorods.

Our efforts in ZnO nanorod growth and characterization have generated several publications in premier journals (including one feature article with cover art), many invited and contributed talks, and a First-place “Art as Science” award at the Materials Research Society Spring 2005 meeting.

Significance—The ability to synthesize controlled ZnO nanostructures is the foundation of our current work on next-generation solar cells based on ZnO nanostructures and conducting polymer matrices. These hybrid solar cells are targeted for light-weight, portable applications, such as consumer electronics.

Sponsors for various phases of this work include: Laboratory Directed Research & Development, Truman Fellowship, and DOE Office of Basic Energy Sciences

Contact: Julia W. P. Hsu, Surface & Interface Sciences, Dept. 1114
Phone: (505) 284-1173, Fax: (505) 844-5470, E-mail: jwhsu@sandia.gov

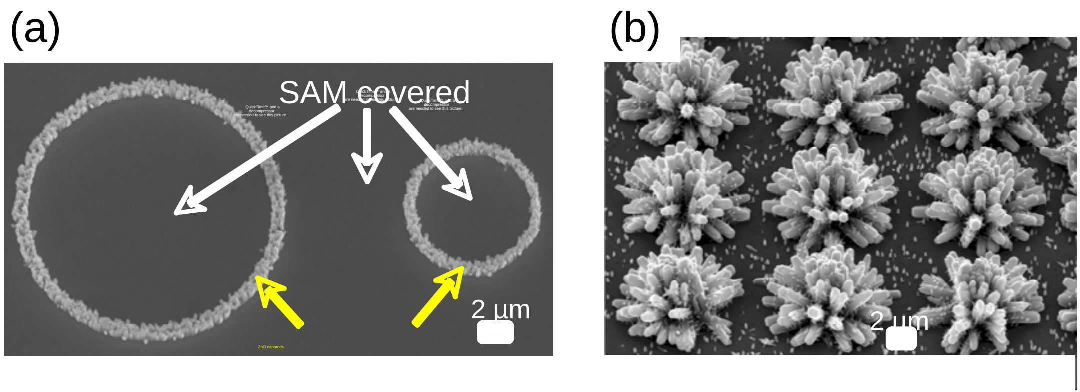

Figure 1. Solution-grown ZnO nanostructures on Ag substrates containing a molecular template. (a) Oriented nanorods assembled in 1.4-micron width rings. (b) Complex ZnO nanostructures clustered at 10-micron square lattices.

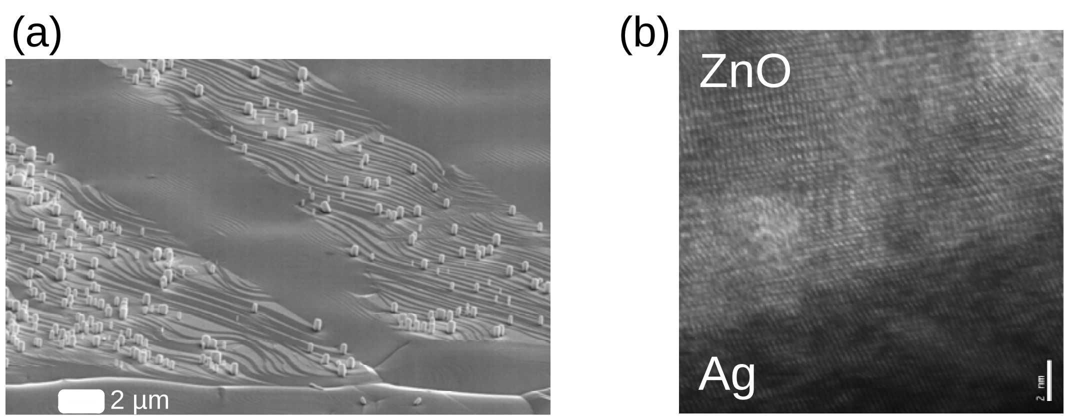

Figure 2. (a) Preferential nucleation of ZnO nanorods on (111) oriented Ag grains. (b) Abrupt and facetted ZnO-Ag interfaces.

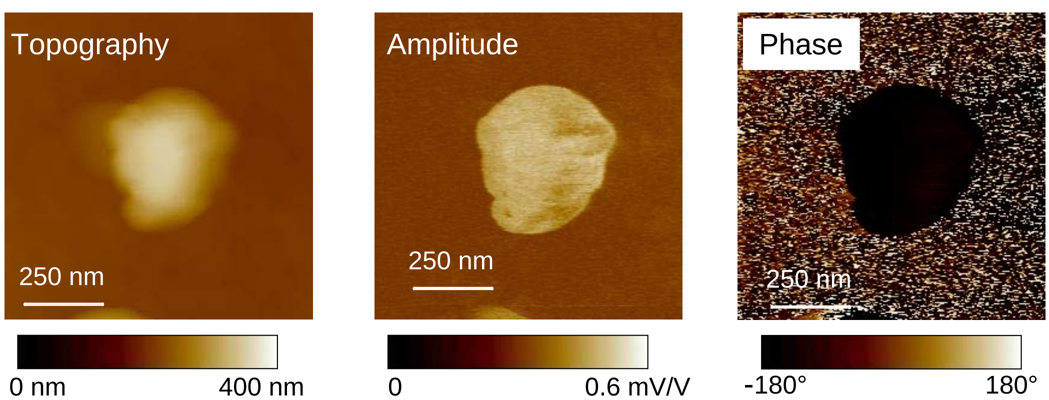

Figure 3. Piezoelectric force microscopy images of a single ZnO nanorod. 0° phase indicates <000$\bar{1}$> orientation and ±180° phase indicates <0001> orientation.